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(54) **Adhesive composition1.**

(57) A heat-curable adhesive composition comprising a mixture of substantially solid particles of a first reactive component with separate substantially solid particles of at least a second reactive component, the first and second reactive components being capable of reacting together to effect curing when the composition is heated to the curing temperature and the particles having a size distribution in which not more than 40% by weight of the particles are less than 50 micrometres in size and substantially all the particles are less than 300 micrometres in size.

The specified particle size range is especially advantageous when the composition is to be used on a heat-shrinkable article to form a cured adhesive bond upon heat-shrinkage of the article about an object.

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## ADHESIVE COMPOSITION

This invention relates to adhesive compositions and especially to adhesive compositions that may be used with dimensionally heat-recoverable articles

A heat-recoverable article is an article the dimensional configuration of which may be made substantially to change when subjected to heat treatment

5 Usually these articles recover on heating, towards an original shape from which they have previously been deformed but the term "heat-recoverable", as used herein also includes an article which, on heating, adopts a new configuration, even if it has not been previously deformed.

In their most common form, such articles comprise a heat-shrinkable sleeve made from a polymeric material exhibiting the property of elastic or plastic memory as described, for example in U.S. Patents 10 2.027.962 3.086.242 and 3.597.372. As is made clear in, for example, U.S. Patent 2.027.962, the original dimensionally heat-stable form may be a transient form in a continuous process in which, for example, an extruded tube is expanded, whilst hot, to a dimensionally heat-unstable form but, in other applications, a preformed dimensionally heat-stable article is deformed to a dimensionally heat-unstable form in a separate stage.

15 In the production of heat-recoverable articles the polymeric material may be cross-linked at any stage in the production of the article that will enhance the desired dimensional recoverability. One manner of producing a heat-recoverable article comprises shaping the polymeric material into the desired heat-stable form, subsequently cross-linking the polymeric material, heating the article to a temperature above the crystalline melting point or, for amorphous materials the softening point, as the case may be, of the 20 polymer, deforming the article and cooling the article whilst in the deformed state so that the deformed state of the article is retained. In use, since the deformed state of the article is heat-unstable, application of heat will cause the article to assume its original heat-stable shape.

In other articles as described, for example in British Patent 1.440.524, an elastomeric member such as an outer tubular member is held in a stretched state by a second member, such as an inner tubular 25 member, which, upon heating weakens and thus allows the elastomeric member to recover.

Heat-recoverable articles are often used in applications in which they are required to be coated with an adhesive. In certain applications such articles are required to be used with curable adhesives in order that the bonds so formed will exhibit good performance at high temperatures and/or under high loads. One 30 example of such an application is where hollow heat-recoverable moulded articles having one or more outlets (often called end-caps, boots, transitions or udders) are used to enclose various parts of cable harnesses. Until recently it had not been possible to pre-coat such articles with a heat-curable adhesive that would cure when the article was recovered because the relatively low recovery temperatures of the articles e.g. about 100 to 130°C and the relatively short recovery times, e.g. up to 2 minutes, were incompatible with an adhesive that would have an acceptably long storage life, and so it was necessary to coat the 35 articles with a two-component curable adhesive immediately prior to installation.

Recently, it has been proposed in U.K. Patent Specification No. 2.104.800A, the disclosure of which is incorporated herein by reference, that heat-recoverable articles may be coated with a heat-curable adhesive in which the reactive components are in the form of separate particles that are mixed together. It has been 40 observed that such adhesives exhibit a synergistic increase in rate of cure when used with a heat-recoverable article, which enables them to cure sufficiently rapidly when the article is recovered and yet have an acceptably long storage life.

Although the coated articles so formed work well in practice it has been found that the functional performance of the adhesives may be considerably improved.

According to one aspect, the present invention provides a heat-curable adhesive composition which 45 comprises a plurality of reactive components that will react together to cure the adhesive composition, the components existing separately from one another in the form of solid particles that are mixed together and which will fuse when heated, the particles having a size distribution in which not more than 40%, preferably not more than 35% and especially not more than 30% by weight of the particles are less than 50 micrometres in size and substantially all the particles, that is to say at least 90% and especially at least 50 95% by weight, are less than 300 micrometres in size.

Preferably not more than 60%, more preferably not more than 50% and especially not more than 40% by weight of the particles are less than 75 micrometres in size, and preferably not more than 70%, especially not more than 60% by weight of the particles are less than 100 micrometres in size. The preferred particle size distributions are those in which the particles have a weight average particle size in the range of from 75 to 125 micrometres.

It has been observed that the correct choice of particle size distribution is important in determining whether or not the adhesive will exhibit the required high temperature performance properties. For example the German Military V.G. Specification No. 95343 part 14, for testing harness systems, issued by the Bundesamt für Wehrtechnik und Beschaffung includes a static load test in which the bonds between the harness components are subjected to a 5 kg force load at 100°C for 4 hours without failing or without shearing by more than 5 mm. It had been considered that particulate curable adhesives having the finest particle size distributions commensurate with adequate storage stability would exhibit the best performance on the basis that the finer the particles the greater their surface area/volume ratio and the more intimate their mixing would be, and indeed this belief was borne out when the adhesives were tested using conventional lap-shear test methods. However, surprisingly it has been observed that although lap-shear values improve as the adhesive particle size is reduced, such adhesives fail the V.G. static load test completely and that only those adhesives having relatively coarse particles according to this aspect of the invention pass the test. The reason why this is so is not known. Heat-curable adhesives which may be suitable for the present invention include, those described in British Patent Application 2104800.

Preferred reactive components are those which are capable of reacting together at ambient temperatures, e.g. when forced into intimate contact by shear forces or when dissolved in a mutual solvent.

Preferably one of the reactive components is a thermoplastic epoxy resin, for example an epoxy resin based on a bisphenol A or an epoxy novolak resin, in which case the other reactive component may comprise a carboxylic acid, phenolic resin, anhydride or isocyanate or a material having reactive amine groups. Preferably the adhesive is based on a thermoplastic epoxy resin as one reactive component and a material containing reactive amine groups as the or at least one other reactive component. The material containing free amine groups may be a polyamide, for example one that is used conventionally as a hot-melt adhesive. These polyamides are characterized by the fact that their amide linkages are separated by an average of at least fifteen carbon atoms and have amorphous structures in contrast with the more highly crystalline, fibre forming polyamides such as nylon 6 or nylon 6.6. The polyamides preferably have an amine number of at least 5, the upper limit for the amine number being determined by the fact that as the amine number increases the polyamides become liquid at lower temperatures.

Alternatively or in addition the or at least one material having reactive amine groups is one based on a polymer that is the same as or similar to that on which the epoxy resin is based. For example, and preferably, the or at least one material containing reactive amine groups is an adduct of the epoxy resin that is used with a compound containing reactive amine groups, preferably with an aliphatic diamine or triamine and especially with ethylene diamine or ethylene triamine.

It has been found that the use of an epoxy-amine compound adduct as the other reactive component or one of the other reactive components can significantly improve the cure rate of the adhesive in relation to its storage life, thereby permitting the storage life of the adhesive or the cured properties thereof to be improved or allowing greater freedom to alter the adhesive in order to optimise its other properties. Thus, according to another aspect, the invention provides a heat-curable adhesive composition, which comprises a plurality of reactive components that will react together to cure the adhesive composition, the reactive components existing separately from one another in the form of particles which are mixed together and which will fuse when heated, at least one of the reactive components being a thermoplastic epoxy resin and the or at least one other reactive component being an adduct of the epoxy resin with a compound containing reactive amine groups.

The adduct may, if desired, be used as the sole reactive component that contains reactive amine groups although it is preferred for the adduct to be present in combination with at least one other reactive amine group such as a thermoplastic polyamide for example to improve flexibility of the adhesive. Preferably the adhesive contains from 30 to 90% and especially from 40 to 80% by weight adduct based on the total weight of the adduct and other reactive amine group containing components.

Chemical curing accelerators may also be present in the adhesive, either blended with one of the reactive components or as separate particles. Examples of accelerators include dimethylaminopyridine, tris (dimethylaminomethyl) phenol, tin octoate, imidazole or imidazole derivatives such as salts, substituted imidazoles or metal complexes thereof.

A number of inert components may be incorporated in the compositions as long as they do not adversely affect the increase in rate or level of cure of the adhesive composition. Also it is preferred if they do not adversely affect the storage life of the adhesive.

Inert components that may be incorporated in the adhesive include plasticisers such as phthalates or rosin esters, thermoplastic or thermosetting polymers, cured or uncured rubbers, inorganic materials to modify the properties of the uncured or cured adhesive such as reinforcing fillers, reinforcing fibres or microspheres, or tackifiers and the like. The other components, whether organic or inorganic, may be in any appropriate physical form, for example they may be in the form of powder, flake or fibers, or they may be compounded with one or more of the reactive components, and are preferably present in an amount of from 5 to 50 percent by weight based on the total weight of the composition.

Electrically conductive fillers, e.g. metal flakes may be incorporated in the adhesive to provide electrical continuity, e.g. when the adhesives are used to seal parts of an electromagnetically shielded electrical wiring harness, as discussed hereinafter.

Preferably the adhesive compositions according to the invention contain a polymeric binder in order to prevent the adhesive crumbling off the surface to which it is applied before it is cured. This is a particular problem when using particulate adhesives according to the invention that are applied to heat-recoverable articles since the heat-recoverable articles, which will usually be in an expanded configuration, are generally easily deformable and are usually subjected to various degrees of mechanical abuse in storage. It has surprisingly been found that useful degrees of cohesion can be achieved without unacceptably affecting the curing performance.

Thus, another aspect of the invention provides, a cohesive flexible substantially solid heat-curable adhesive coating formed from a mixture of substantially solid particles of a first reactive component with separate substantially solid particles of at least a second reactive component in a solution of not more than 15% by weight, based on the total dry weight of the coating, of a binder, the binder solution solvent being substantially a non-solvent for the first and second reactive components which are present in the dry coating as substantially unreacted separate particles capable of reacting together to effect curing when the coating is heated to the curing temperature. Preferably the binder content will be less than 10% more preferably less than 5%, and even more preferably less than 2.5%, and preferably at least 1% by weight. It will be understood that references to "substantially solid" particles exclude liquid filled microcapsules and are intended to mean particles which are substantially non-flowable (to render the coating storage stable) at the intended maximum storage temperature.

It is preferable to apply the adhesive onto the article by forming a dispersion of the reactive components in a non-solvent, either spraying or dip-coating the adhesive, in which case the binder should be soluble in the non-solvent, and then removing the non-solvent by evaporation. The preferred binders for use with the adhesive are unsubstituted or substituted polyalkylene oxides that are soluble in water and water-soluble polyvinyl acetate polymers having substantially no free hydroxyl groups. The preferred binders are the polyalkylene oxides and especially polyethylene oxide. It has been found that most solvents with the exception of water, water based solvents and light aliphatic solvents such as hexane, solubilise one or other of the reactive components at least to some extent and so are unsuitable, while those binders that were considered for use with acceptable non-aqueous solvents lead to unacceptably poor cured adhesives. When water is used as a non-solvent for the dispersion the alkylene oxide and vinyl acetate polymers mentioned above produced adhesives having the best properties although it is envisaged that some other water-soluble polymers having substantially no free hydroxyl groups may be suitable. Whatever polymer is used for the binder, it is preferred that it be thermoplastic having a melting or softening point no higher than 20°C above the highest melting or softening point of the reactive components and preferably no higher than the highest melting or softening point of the reactive components, in order to ensure that the binder melts completely when the adhesive is cured. When the adhesive is used in conjunction with a heat-recoverable article, the binder should have a melting or softening point no higher than the recovery temperature of the article and preferably no higher than 20°C below the recovery temperature of the article, whatever the melting point of the reactive components may be.

Thus according to another aspect, the invention provides a heat-curable adhesive composition which comprises:

(a) a plurality of reactive components that will react together to cure the adhesive composition, the components existing separately from one another in the form of solid particles which are mixed together and which will fuse when heated and

(b) a polymeric binder comprising a substituted or unsubstituted polyalkylene oxide that is soluble in water.

Preferably the binder is present in the adhesive compositions only to relatively low levels, for example up to 15% by weight, more preferably up to 10% by weight and especially up to 5% by weight, based on the total weight of the adhesive composition, in order that the binder does not adversely affect the cured properties of the adhesive. It has been found that even though the quantity of binder used in generally

significantly below the quantities used in the prior art, the uncured adhesive does not show any unacceptable tendency to crumble off the article during storage. Preferably the binder is present in quantities of at least 0.1%, more preferably at least 0.2% and especially at least 0.5% by weight, the optimum binder level being about 2% by weight, based on the total weight of the adhesive composition.

- 5 In addition, the use of relatively low quantities of binder reduces the adverse affect than binders generally have on the performance of the adhesives and, in particular, on their high temperature performance.

Preferably the adhesive composition is as described above.

- The adhesive compositions according to the invention are particularly useful as latent curing adhesives  
10 for dimensionally heat-recoverable articles in view of their good stage life and their relatively rapid cure rate during recovery of the article. In order to maximise the cure rate of the adhesive, it is preferred that the or each reactive component has a melting or softening point that is no higher than 20°C below the recovery temperature of the article. Preferred articles with which the adhesives are used include open-ended hollow articles which are, for example, used for enclosing parts of electrical harness and the like, although the  
15 adhesives may be used with other heat-recoverable articles and, if desired, with articles that are not heat-recoverable. Such articles, which are often termed end-caps, boots, transitions or udders, depending on the number of outlets, are preferably coated with the adhesive on their internal surface in the region of the or each outlet, but not in the central region. This may be achieved by applying the adhesive by a dip-coating method in which the outlet of the article is dipped in an aqueous dispersion of the adhesive, or if possible a  
20 dispersion in another non-solvent, and the water or other non-solvent is allowed to evaporate off.

The following Examples illustrate the invention:

#### Examples 1 to 3

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A heat curable adhesive composition was formed based on the following composition:

COMPONENTS		Trade name	Parts by weight
1	Epoxy resin	Epikote 1001 (Ex Shell)	100
2 (cure agent)	Polyamide	Macromelt 6071 (Ex Henkel)	25
	Epoxy diamine adduct	EDA 870 (Ex Anchor Chemi- cals	75
	Aluminosilicate filler		20
	Carbon black		2
3 (flexibilizer)	Acid/Ethylene/vinyl acetate terpolymer	CXA 2002 (Ex du Pont)	10
4 (binder)	Polyethylene oxide	Polyox (Ex Union Carbide	2.4

Component 2 was formed by melt blending and then grinding on a fanbeater mill at room temperature until the desired particle size distribution is reached by adjusting the grinding conditions. Component 1 was also ground on a fan beater mill in the same manner as component 2. Component 3 was cryogenically ground, and components 1, 2 and 3 were then tumble blended. Component 4 was dissolved in a quantity of water equal to the total weight of the other components to form a 2% solution to which was added the powdered components 1, 2 and 3 to form an aqueous dispersion of the complete adhesive.

This dispersion was applied to a standard Raychem 202K153 boot formed from Raychem -25 material by a dip-coating method, and the adhesive was dried in air at room temperature for 6 hours followed by drying under vacuum at room temperature for a further 7 hours. The resulting adhesive thickness was 0.6 to 0.7 mm.

The boot was recovered about a cable and the adhesive joint was tested by means of the static load test at 100°C specified in the V.G. Specification No. 95343 part 14 as well as by the lap shear test according to A.S.T.M. D.1002. In the static load test, the cable and boot are subjected to a 5 kg load at 100°C for 4 hours and the length that the cable had pulled out of the boot or the time to failure of the bond is recorded. For those bonds in which the cable had not been pulled out of boot, the strength of the resulting bond is then measured at room temperature. The results are shown in Table I for three adhesives that had differing particle size distributions. The particle size distributions of the adhesives are given in Table II.

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TABLE I

Example	Particle size	100°C lap shear strength N(25mm) <sup>-2</sup>	V.G. static load test (100°C) strength and pullout of passes time to failure of failures
1	Coarse	140	5 passes mean pullout = 1mm mean strength - 453N
2	Medium	250	1 pass pullout = 1mm strength - 360N  2 failures failure time 1.5 hr and 1 hr
3	Fine	300	All fail within 10 minutes

TABLE II

Weight percentage of particles less than

Example	50 um	75 um	100 um	150 um	300 um
1	25	35	49	72	96
2	48	61	81	95	100
3	55	81	100	100	100

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Examples 4 to 7

55 As adhesive composition was prepared according to Example 1 with the exception that the curing agent (component 2) was formed from a blend of two polyamides (80 parts Macromelt 6071 and 20 parts Versamid 140), and that the binder content was varied between 0 and 4%. The adhesive was applied to a - 25 Raychem moulded part as an aqueous dispersion and dried and then used to form a bond between it and either a cable having a Raychem DR-25 jacket or an adaptor. The room temperature peel strength was

measured according to V.G. 95343 part 14 Section 2.2 and 2.3. The results are shown in table III from which it can be seen that the cable peel strength increases considerably for small quantities of polyethylene oxide binder. In addition, the moulded parts were subject to a further test before being recovered onto the cable, in which they were squeezed to 75% of their original diameter in one direction and then rotated  
5 through 120° about their axis before being squeezed again. None of the adhesive was observed to fall off the part in any instance in which the binder level was between 1 and 4%.

Examples 8 to 10 (comparison)

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Examples 5 to 7 were repeated with the exception that the binder was styrene-isoprene-styrene rubber and the adhesive dispersion was formed in hexane as the non-solvent. The results for the cable peel and adaptor peel strength are also shown in table III and show that the rubber based binder gave significantly inferior performance.

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TABLE III

Example	Binder content (weight %)	Cable peel (N)	Adaptor peel (N)
4 (comparison)	0	63	132
5	1	112	130
6	2	113	110
7	4	111	150
8 (comparison)	1	25	20
9 (comparison)	2	40	43
10 (comparison)	4	29	38

Examples 11 and 12

In order to demonstrate the improved storage stability and curing of the adhesive formulations that contain an adduct, the following two adhesive formulations were prepared by the method described in Example 1.

Example	Components	Parts by weight
11	(1) Epoxy      Epikote 1001	100
	(2) Cure agent      Polyamide - Macromelt 6071	50
	adduct - EDA 870	50
	(3) Flexibiliser      CXA 2002	20
12	(1) Epoxy      Epikote 1001	100
	(2) Cure agent      Polyamide Macromelt 6071	80
	Polyamide Versamid 140	20
	(3) Flexibiliser      CXA 2002	20

The minimum viscosity of the adhesives with respect to time were measured at 100°C using a Ferranti-Shirley Viscometer both when fresh and after a few weeks storage at ambient temperature.

For Example 11 the minimum viscosity on heating reduced from 900 poise when fresh to 464 poise after 10 weeks at 40°C whereas for Example 12 the minimum viscosity increased from 260 poise when fresh to 1125 poise after 12 weeks storage at 40°C. indicating that the adduct did not cure to any significant extent on storage whereas the polyamide based one did.

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## Claims

1. A heat-curable adhesive composition comprising a mixture of substantially solid particles of a first  
10 reactive component with separate substantially solid particles of at least a second reactive component, the first and second reactive components being capable of reacting together to effect curing when the composition is heated to the curing temperature, and the particles having a size distribution in which not more than 40% by weight of the particles are less than 50 micrometres in size and substantially all the particles are less than 300 micrometres in size.
- 15 2. A composition as claimed in claim 1, which includes a polymeric binder, which is substantially unreactive with the first and second reactive components at least at ambient temperatures.
3. A composition according to claim 2 comprising not more than 15% by weight, preferably not more than 5% by weight, of the binder.
4. A composition according to claim 3, comprising 0.5 to 5% by weight of the binder.
- 20 5. A composition according to claim 3 or 4, comprising not more than 2.5% by weight of the binder.
6. A composition according to any of claims 2 to 5 comprising at least 1% by weight of the binder.
7. A composition according to any of the preceding claims wherein the particles of the first reactive component are connected to those of the second reactive component substantially only by the said binder.
8. A composition as claimed in any of the preceding claims, wherein one of the reactive components is  
25 a thermoplastic epoxy resin.
9. A composition as claimed in claim 8, wherein the or at least one other reactive component is a material having reactive amine groups.
10. A composition as claimed in claim 8 and 9, wherein the or at least one material having reactive amine groups in an adduct of the epoxy resin with a compound containing reactive amine groups.
- 30 11. A composition as claimed in claim 9 or 10, wherein the material having reactive amine groups is a polyamide.
12. A compositions claimed in claim 9 or 10, wherein the material containing reactive amine groups is ethylene diamine or ethylene triamine.
13. A composition as claimed in any one of the preceding claims, wherein the particles have a size  
35 distribution in which not more than 30% by weight of the particles are less than 50 micrometres in size.
14. A composition as claimed in any one of the preceding claims, wherein not more than 60% by weight of the particles are less than 75 micrometres in size.
15. A composition as claimed in claim 14, wherein not more than 50% by weight of the particles are less than 75 micrometres in size.
- 40 16. A composition as claimed in any one of the preceding claims, wherein the particles have a weight average particle size in the range of from 75 to 125 micrometres.
17. A composition according to any of the preceding claims, wherein the first and second reactive components are capable of reacting together when brought into reactive contact at ambient temperatures.
18. A composition according to any of the preceding claims, wherein electrically conductive solid  
45 particles are incorporated to render the cured composition electrically conductive.
19. A method of manufacturing a coating of a composition according to any of the preceding claims, comprising applying to a substrate a dispersion of the said mixture of the first and second reactive components and a binder in a liquid which is substantially a non-solvent for the reactive components, and removing the liquid from the dispersion.
- 50 20. A method according to claim 19, wherein the particles of the first reactive component are freely moveable in the dispersion relative to the particles of the second reactive component, so as to produce a coating composition according to claim 7.
21. A method as claimed in claim 19 or 20, wherein the adhesive composition is applied to the surface of the article from an aqueous dispersion.
- 55 22. A method as claimed in claim 19, 20 or 21, wherein the adhesive composition is applied to the surface of the article by a dip-coating method.
23. A coating made by a method according to any of claims 19 to 22.

24. A dimensionally heat-recoverable article having on at least part of a surface thereof, an adhesive composition as claimed in any one of claims 1 to 18, or a coating of such a composition as claimed in claim 23.

25. An article as claimed in claim 24 which is a hollow article with at least one opening to the exterior and has the adhesive composition on the inner surface thereof in the region of the or each opening.

26. An article as claimed in claim 24 or 25, wherein the or each reactive component has a melting or softening point no higher than 20°C below the recovery temperature of the article.

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(54) Heat recoverable article.

(57) A dimensionally recoverable article, preferably a heat-recoverable article, has on at least part of a surface thereof an adhesive composition that will cure by reaction of a plurality of mutually reactive components. The components are in the form of particles which are mixed together and which will fuse when heated. Preferred adhesives are based on combinations of an epoxy with a polyamide, carboxylic acid, phenolic resin or blocked isocyanate curing agent.

The particulate adhesives show a synergistic increase in rate and/or level of cure when used in conjunction with a recoverable article.

EP 0 74 218 A1



This invention relates to dimensionally-recoverable articles, especially dimensionally heat-recoverable articles and to adhesives suitable for use therewith.

5       A heat-recoverable article is an article the dimensional configuration of which may be made substantially to change when subjected to heat treatment.

10       Usually these articles recover, on heating, towards an original shape from which they have previously been deformed, but the term "heat-recoverable", as used herein, also includes an article which, on heating, adopts a new configuration, even if it has not been previously deformed.

15       In their most common form, such articles comprise a heat-shrinkable sleeve made from a polymeric material exhibiting the property of elastic or plastic memory as described, for example, in U.S. Patents 2,027,962; 3,086,242 and 3,957,372. As is made clear in, for example, U.S. Patent 2,027,962, the original dimension-  
20       ally heat-stable form may be a transient form in a continuous process in which, for example, an extruded tube is expanded, whilst hot, to a dimensionally heat-unstable form but, in other applications, a preformed dimensionally heat stable article is deformed  
25       to a dimensionally heat-unstable form in a separate stage.

In the production of heat recoverable articles, the polymeric material may be cross-linked at any stage in the production of the article that will enhance the desired dimensional recoverability. One manner of  
5 producing a heat-recoverable article comprises shaping the polymeric material into the desired heat-stable form, subsequently cross-linking the polymeric material, heating the article to a temperature above a transition temperature thereof, for example, the  
10 crystalline melting point or, for amorphous materials the softening point, as the case may be, of the polymer, deforming the article and cooling the article whilst in the deformed state so that the deformed state of the article is retained. In use, since the deformed  
15 state of the article is heat-unstable, application of heat to raise the temperature above the transition temperature will cause the article to assume its original heat-stable shape.

Where the term "recovery temperature" in connection with heat-recoverable articles is used herein,  
20 it is intended to refer to the transition temperature above which the article recovers even if some small degree of recovery is exhibited at temperatures slightly below the transition temperature.

25 In other articles, as described, for example, in British Patent 1,440,524, an elastomeric member such as an outer tubular member is held in a stretched state by a second member, such as an inner tubular member, which, upon heating weakens and thus allows the elastomeric member to recover.  
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Articles of this type have, in recent years, become widely used in a number of applications, for example for protecting objects such as electrical cables and cable splices or metal pipes from corrosion or other damage, for example damage caused by penetration of moisture. For this reason many heat-recoverable articles are provided with a coat of adhesive or sealant.

One problem that is associated with the provision of adhesives on heat-recoverable articles is that, because the heat required to melt or otherwise activate the adhesive is usually supplied by heating the external surface of the heat-recoverable article, the temperature to which the adhesive is heated will be considerably lower than that of the external surface of the article due to the relatively poor thermal conductivity of the materials from which the heat-shrinkable article is formed. Thus, for example, where the heat-shrinkable article is formed from a cross-linked polyethylene, the external surface of the article may be heated up to about 250°C in order to raise the adhesive temperature to only 100°C, and, in this case, no further heating of the article would be possible without damaging the article. Also, in many cases, the maximum temperature to which the adhesive can be raised is restricted by the type of substrate that is being covered. For example, where the substrate is a metal pipe, the thermal conductivity and size of the pipe cause it to act as a heat-sink and effectively limit the adhesive temperature and, where the substrate comprises an uncrosslinked polymer as is often the case

with electrical cable jackets, the adhesive temperature often cannot be raised above about 100 to 120°C without damaging the cable jacket.

5        Whilst hot-melt adhesives or mastics can be used in a number of applications, the maximum temperature to which the article may be subjected after installation is usually limited to the melting or softening point of the adhesive.

10       The present invention provides a dimensionally recoverable article, preferably a dimensionally heat recoverable article, having, on at least part of a surface thereof, an adhesive composition that will cure by reaction of a plurality of mutually reactive components, the components existing separately from one  
15       another in the form of solid particles which are mixed together and which will fuse when heated.

20       Preferably the components are such that, if they are brought together into intimate contact for example by dissolving them in a common solvent, they will react together even at room temperature to form a cured product so that curing of the adhesive composition on the article during storage is prevented substantially solely by the separation of the particles of each component.

25       In a number of cases it has been found that when the heat-recoverable article according to the invention is recovered onto a substrate, the adhesive will cure sooner than if it is heated on its own to the same



temperature, or will cure at a significantly lower temperature than it will when heated on its own. Thus it has been found that it is possible, according to the invention, to provide an adhesive coated heat-recoverable article in which the adhesive can be cured by heating the article to its recovery temperature for periods in the range of the recovery time of the article, but which will also have good storage life.

The rate of curing of curable adhesives at elevated temperatures is linked to their rate of curing at ambient temperatures, and hence their storage life, by the Arrhenius equation which effectively imposes a limit on the rate of cure of an adhesive at the usual recovery temperature of a heat-shrinkable article (about 100 to 120°C) for any given storage life at ambient temperatures or vice versa. It can be shown from the Arrhenius equation that any curable adhesive that cures sufficiently rapidly at the recovery temperature of the article should suffer from a poor storage life or that an adhesive that does have a long storage life should not cure sufficiently rapidly at the recovery temperature of the article. However, according to the invention it is possible to overcome this problem by virtue of the synergistic increase in the rate of curing of certain adhesives when used in conjunction with a recoverable article.

This synergistic effect is most pronounced when the fusion temperature of the components is in the

region of the recovery temperature of the article or the temperature to which the adhesive is heated when the article is recovered. Preferably the fusion temperature is not more than 50°, especially not more than 30° and most especially not more than 10°C above the recovery temperature of the article. Also, not more than one, and especially none, of the components has a fusion temperature of less than 50°C. Each of the components preferably has a fusion temperature in the range of 70 to 120°C and most preferably from 70 to 100°C, and, instead or in addition, each has a fusion temperature that differs from the fusion temperature of the or each other reactive component by not more than 30°C.

In most instances the components will melt or soften at their fusion temperature although the term is intended to include sublimation of one or more components if this occurs.

In many cases the reactive components will soften and flow or otherwise fuse over a temperature range and the softening characteristics of the components may be observed by thermomechanical analysis (TMA) as described in "Thermal Analysis" by T. Daniels published by Kogan Page 1973. Accordingly, the fusion temperature or the melting point of the reactive components of the adhesive is defined herein as being the temperature at which the TMA probe has penetrated to 60% of the total thickness of the material, usually referred to as  $T_{60}$ . The TMA data described herein were obtained using a 6.35mm diameter flat profile probe loaded with a 50

gramme weight and by increasing the temperature of the material at a rate of 10°C per minute. Preferably the temperature at which reactive components of the adhesive initially become soft referred to as  $T_i$  on the TMA plot) is not more than 30°C below and especially not more than 25°C below the melting point ( $T_{60}$ ) of the components so that the difference between the maximum storage temperature and the minimum curing temperature can be reduced as far as possible.

Another synergistic effect that may be shown by the articles according to the invention, either instead of or in addition to the increase in rate of cure of the adhesive is an increase in the level of curing of the adhesive as compared with the adhesive on its own. The increase in level of curing leads to improved properties such as solvent resistance and improved high temperature properties such as high temperature shear strength.

The level of cure of the adhesive may be measured in a number of ways. For example, it may be measured as an increase in the  $T_{60}$  (as defined above) or, more preferably the  $T_{80}$  of the adhesive, where  $T_{80}$  is defined as the temperature at which the TMA probe has penetrated to 80% of the total thickness of the adhesive. In some cases the composition will cure sufficiently to prevent the probe penetrating it by 80% in which case the total depth of penetration is a better measure of cure. Another measure of the level of cure of the adhesive is its gel content which is measured by weighing a quantity of the adhesive into an extraction

thimble, refluxing the adhesive for 5 to 8 hours with a solvent (e.g. 1,2-dichloroethane or tetrahydrofuran), drying the thimble in an oven for 24 hours to evaporate the solvent and, after leaving the dried thimble in the atmosphere for a further 24 hours reweighing the thimble. The gel content is then defined as the final weight of the adhesive (which is insoluble) expressed as a percentage of the initial weight of the adhesive.

The adhesive cures, as stated above, by reaction of a plurality of mutually reactive components. The phrase "mutually reactive components" is defined herein as meaning components which, when mixed together in their particulate form, will react together at the fusion temperature thereof or at least at the highest fusion temperature thereof to form a composition having a  $T_{80}$  value that is at least 20°C, preferably at least 30°C and especially at least 40°C above the initial fusion temperature of the blend. Preferably the components will exhibit a gel content of at least 20%.

According to another aspect, the invention provides a method of enclosing at least part of a substrate, which comprises:

- (a) positioning thereon a dimensionally-recoverable article such that an adhesive composition is disposed between the article and substrate, the adhesive composition comprising a plurality of mutually reactive components that exist separately from one another

in the form of solid particles which are mixed together and which will fuse when heated; and

- 5 (b) recovering the article about the substrate and heating the adhesive to fuse the particles.

There is essentially no limit on the particle size of the reactive components in that the articles can still show a synergistic increase in rate and/or level  
10 of cure even with very large particles although the absolute value of the cure rate will decrease with large particles. Preferably the reactive components will have a weight average particle size of not more than 1000, especially not more than 500 and most  
15 especially not more than 300 micrometres. Preferably the reactive components have a weight average particle size of at least 1, more preferably at least 5 and especially at least 10 micrometres. The particle size of the reactive components may conveniently be adjusted  
20 by sieving the particles through an appropriately sized mesh in which case it is preferred that the particulate components are substantially free of particles greater than 500 micrometres in size. The preferred particle size ranges are from 5 to 300 and especially 10 to 200  
25 micrometres.

The adhesive composition may, if desired, consist solely of the reactive components although it is preferred for it to include one or more inert components. The inert components may be present with the

reactive components in the particles, or may be mixed with the particles as a separate phase or both. For example, the adhesive may comprise a particulate curable resin such as an epoxy resin, preferably one  
5 based on bisphenol A or on epoxy novolak resin, as one component and a particulate curing agent such as an amine, carboxylic acid, phenolic resin or isocyanate curing agent as the other. The curing agent may itself be polymeric for example it may be a polyamide having  
10 free amino groups or a carboxylated polymer such as an acid terpolymer, in which case the particles of the curing agent need not contain any inert component. If the curing agent is not polymeric, for example an organic peroxide or other free radical initiator, it  
15 may be desirable for it to be blended with a polymeric material, e.g. a polyester or a reactive or unreactive polyamide before comminution. The curable resin may, instead, comprise a polyamide having free amine groups, in which case the curing agent preferably comprises a  
20 material having free or blocked isocyanate functional groups, e.g. a cresyl blocked isocyanate.

The polyamides that are most suitable for forming one of the components are those that are conventionally used as hot-melt adhesives. These polyamides are  
25 characterized by the fact that their amide linkages are separated by an average of at least fifteen carbon atoms and have amorphous structures in contrast with the more highly crystalline, fibre forming polyamides such as nylon 6 or nylon 6.6. The polyamides prefer-  
30 ably have an amine number of at least 5, the upper limit for the amine number being determined by the fact

that as the amine number increases the polyamides become liquid at lower temperatures.

5 Chemical curing accelerators may also be present in the adhesive, either blended with one of the reactive components or as separate particles. Examples of accelerators include dimethylaminopyridine, tris (dimethylaminomethyl) phenol, tin octoate, imidazole or imidazole derivatives such as salts, substituted imidazoles or metal complexes thereof.

10 A number of inert components may be incorporated in the compositions as long as they do not adversely affect the increase in rate or level of cure of the adhesive composition. Also it is preferred if they do not adversely affect the storage life of the adhesive.

15 Inert components that may be incorporated in the adhesive include plasticisers such as phthalates or rosin esters, thermoplastic or thermosetting polymers, cured or uncured rubbers, inorganic materials to modify the properties of the uncured or cured adhesive such as  
20 reinforcing fillers, reinforcing fibres or microspheres, or tackifiers and the like. The other components, whether organic or inorganic, may be in any appropriate physical form, for example they may be in the form of powder, flake or fibres, and are preferably  
25 present in an amount of from 5 to 50 percent by weight based on the total weight of the composition. In a preferred aspect of the invention the adhesive composition contains one or more other components having a softening temperature range (from the initial softening

temperature to  $T_{60}$ ) that is greater than that of the reactive components so that the softening temperature range of the adhesive composition as a whole is greater than that of the reactive components, preferably by at least 5°C. This has the advantage that, whilst the adhesive will cure when heated to only a relatively low temperature above the maximum storage temperature, it will possess cohesive and adhesive strength over a significantly greater temperature range. Alternatively, in some cases where the reactive components have a large softening temperature range it may be desirable to reduce the softening temperature range of the adhesive composition by incorporation of the appropriate components for example tackifier resins such as hydrogenated rosin esters and terpene phenols or polar waxes such as polyamide and polyester waxes.

As examples of other components that may be incorporated in the adhesive compositions, there may be mentioned tacky materials such as pressure sensitive adhesives or mastics, or thermoplastic materials. The components are preferably, although not necessarily, fluid at temperatures below the melting point of the reactive components, but if they are not they should be such as to allow the reactive components to mix together at the recovery temperature of the article.

The articles according to the invention may be formed in a number of configurations depending on the particular use. The articles may be in the form of a tube that has been extruded and expanded radially to render it heat-recoverable, the tube being either in



continuous lengths or discrete pieces and being coated on its internal surface with the adhesive compositions. Alternatively, the articles may be in the form of a sheet or tape that can be wrapped or wound around an object. More complex shapes, commonly referred to as boots, transitions, udders or caps, may be formed by moulding the articles in the desired configuration and then expanding them or by the methods described in our copending U.K. Applications Nos. 8123069 and 8123072 (serial Nos. 2083403A and 2083859A). The present invention is also suitable for the production of wrap-around devices. So called wrap-around devices are employed for sealing, insulating or otherwise protecting a substrate where the use of a preformed tubular article such as a sleeve, is not possible or convenient e.g. in the case where the end of an elongate substrate is not accessible. In general, such wrap-around articles comprise at least a portion thereof which is adapted to be wrapped around a substrate to be covered and secured in tubular form by closure means. Thereafter, the wrap-around closure may be heat-recovered tightly onto the substrate by application of heat. Examples of wrap-around devices are described in U.S. Patents Nos. 3,379,218, 3,455,326, 3,530,898, 3,542,079 and 3,574,318 the disclosures of which are incorporated herein by reference. Another form of wrap-around device in which the curable adhesive may be used is that described in U.K. Patent Application No. 8113486 (serial No. 2076694A) in which the curable adhesive is used to form a layer of sealant that may be peeled away at any desired point to expose a closure adhesive.

- 15 -

Yet another form of wraparound device in which the curable adhesive may be used comprises a dimensionally recoverable cover having two closure portions which can be brought into abutment to form an adhesive bond using the particulate adhesive, but which, after the adhesive bond has been formed, will change in configuration to form a lap joint by recovery of the cover about the substrate. In this device one closure portion may be in the form of an upstanding flange and the other closure portion may be in the form of a further upstanding flange that is bent or folded downwards at its apex so that, after the closure portions have been pushed into abutment and the cover is recovered, the further flange opens out and a lap joint is formed.

Another preferred article according to the invention is in the form of a continuous tape or sheet, one surface of which is coated with the adhesive composition. Such an article may be wound helically around a substrate for example a metal pipe which is preferably pre-heated, and the wound portions of the tape or sheet may be heated to recover the tape or sheet and cure the adhesive. Often it is desired to operate further on the pipe shortly after the protective article has been recovered thereon, for example to bury it in a pre-dug trench and, because of the rapid cure of the adhesive composition, it is possible to perform such operations only a few minutes after the tape or sheet according to the invention has been recovered thereon.

The adhesive composition may be coated on the heat-recoverable article in a number of ways depending on the type of article and adhesive composition. For example, where the article has an open, generally uniform configuration, it may be provided with a layer of tacky material for example pressure sensitive adhesive layer e.g. by spraying or in the form of a tape, and the adhesive composition may be applied as a powder to the pressure sensitive adhesive bearing portions of the article and compressed thereon by application of pressure. Alternatively, the powder may be compressed into a coherent layer and then bonded to the article by means of a tacky material. For either of these methods, pressures in the order of 0.8 MPa (120 p.s.i.) and temperatures of about 15 to 30°C have been found to be most suitable. These methods of applying the adhesive composition are suitable for applications in which the adhesive contains no components other than the particulate reactive components in addition to those in which the adhesive does contain other components. In another method of applying the adhesive composition, the particulate reactive components are mixed with the other components which preferably comprise or include a pressure-sensitive adhesive or a mastic and the whole composition is pressed onto the heat-recoverable article or pressed into a coherent film which is then adhered to the heat-recoverable article, the temperatures and pressures used preferably being the same as those mentioned above.

Yet another method of application, which is suitable for coating the internal surfaces of tubes or moulded articles, comprises spraying the adhesive onto the appropriate parts of the article. The adhesive may  
5 be sprayed in the form of the dry powder onto a surface that is coated with a tacky material, e.g. a pressure sensitive adhesive, or the particulate reactive components may be dispersed in a non-solvent that contains a binder and, after the dispersion is sprayed onto the  
10 article, the non-solvent is allowed to evaporate.

According to yet another aspect, the invention provides an adhesive composition that is novel per se comprising:

- (a) a thermoplastic polyamide having reactive amine groups;  
15
  - (b) a thermoplastic copolymer of an alkene, preferably ethylene, with an ethylenically unsaturated ester of an alkanol and a carboxylic acid, the ester having up to 6 carbon atoms, and optionally one or more acidic  
20 comonomers; and
  - (c) a thermoplastic epoxy resin;
- components (a) and (b) being present in a ratio of from 35:65 to 75:25, preferably from 35:65 to 65:35, more from 40:60 to 60:40 and especially from 45:55 to 55:45  
25 by weight, and component (c) being present in an amount of from 8 to 79 parts per hundred parts of (a) and (b) combined by weight, components (a), (b) and (c) existing separately from one another in the form of particles that are mixed together. In this case each of  
30 components (a), (b) and (c) will react with the other two components when the composition is heated to above the melting points of the components.

Component (b) preferably has an acid number of at least 1 and preferably also has an acid number of less than 100. The term "copolymer" as used herein in connection with component (b) is intended to include  
5 terpolymers and polymers containing four or more comonomers. The preferred comonomers are vinyl acetate and ethyl acrylate optionally with an unsaturated carboxylic acid e.g. acrylic acid. Examples of materials that may be used include those described in U.S.  
10 patent No. 4,018,733 to Lopez et al, the disclosure of which is incorporated herein by reference.

~~The epoxy~~ used for component (c) may comprise any of a number of epoxies for example those based on novolak resins or on bisphenol A, and may have a  
15 wide range of epoxy values provided it remains thermoplastic. Any of the polyamides mentioned above will in general be suitable as component (a).

The components (a), (b) and (c) preferably each has a melting or softening point ( $T_{60}$ ) in the range of  
20 from 60 to 120°C, more preferably from 70 to 120°C and especially from 70 to 100°C.

The adhesives according to the invention have a softening point that increases on application from the melting or softening points of the components, e.g. in  
25 the order of 90 to 95°C to a value of about 130 to 140°C or even higher and so combine low initial application temperatures with relatively high use temperatures. Furthermore, whilst the adhesive exhibits relatively high bond strengths when subject to shear  
30 stresses it also exhibits surprisingly high bond

strengths at high temperatures in the peel mode, e.g. in the order of 80 to 100 N(25mm)<sup>-1</sup> at between polyethylene substrates in contrast with conventional epoxy adhesives which have extremely low peel strengths.

The following Examples illustrate the invention, all parts expressed therein being by weight:

EXAMPLE 1

20 Parts of a cryogenically ground dimerised fatty acid reactive polyamide sold under the trade name "Macromelt 6071" (formerly called "Versamid 871") ( $T_i=60^{\circ}\text{C}$ ;  $T_{60}=67^{\circ}\text{C}$ ) were mixed with 77 parts of a powdered epoxy resin based on bisphenol A sold under the trade name "DER 662" ( $T_i = 47^{\circ}\text{C}$ ;  $T_{60} = 67^{\circ}\text{C}$ ) and 3 parts of powdered dimethylaminopyridine accelerator ( $T_{60} = 105^{\circ}\text{C}$ ). The mixture was graded so that no particles were greater than 300 micrometres in size.

The composition was pressed onto a heat-shrinkable ethylene vinyl acetate sheet having a recovery temperature of  $80^{\circ}\text{C}$  to an amount of 0.75 to 1 kgm<sup>-2</sup>. The ethylene vinyl acetate sheet having a recovery temperature of  $80^{\circ}\text{C}$  to an amount of 0.75 to 1 kgm<sup>-2</sup>. The sheet had a recovery ratio of 3.75:1 and was wrapped around a mandrel that had been preheated to a predetermined temperature in an oven, and the edges of the sheet were secured. The mandrel and sheet had dimensions such that when the sheet recovered onto the mandrel it had recovered by 60% of its total possible recovery. The sheet and mandrel were placed in the oven and strips of the sheet and adhesive were removed after time intervals. As a comparison, samples of the

adhesive were placed in a 1mm thick bakelit pan and were heated in the oven for the same length of time. The comparison samples had a thickness of about 0.8 to 0.9  $\text{kgm}^{-2}$  (corresponding to the initial thickness of adhesive on the shrinkable sheet) and about 1.5  $\text{kgm}^{-2}$  (corresponding to the final thickness of the adhesive on the recovered sheet).

The extent of cure of the adhesive was measured as the gel content. The results are shown in Table I.

10

TABLE I

Oven Temperature = 100°C

	Time (minutes)	Heat Shrink	Gel Content (%)	
			Comparison (0.8-0.9 $\text{kgm}^{-2}$ )	(1.5 $\text{kgm}^{-2}$ )
15	0	0	0	0
	5	27	15	18
	10	25	17	15
	15	26	20	18
	20	39	23	24
20	30	68	42	56

Example 2

An adhesive was prepared by blending 19 parts of a polyamide sold by Henkel under the trade name "Macromelt 6301" (formerly called Versalon 1300) with 19 parts of a reactive polyamide sold by Henkel under the trade name "Macromelt 6071" (formerly called Versamid 871) and the blend was cryogenically ground and sieved to a particle size of less than 300 micrometres. The

$T_{60}$  melting point was 73°C. To the polyamide was added 60 parts of a bisphenol A epoxy resin sold by Shell Chemicals under the trade name "Epikote 1001" (ground and sieved to a particle size of less than 300 microns) ( $T_{60}$  = 50 - 70°C), 2.5 parts of powdered dimethylaminopyridine and 0.3 parts of a silica flow agent.

The adhesive was coated onto a heat-shrinkable crosslinked ethylene vinyl acetate sheet (Elvax 460 - trade name) having a recovery temperature of 80°C and a recovery ratio of 16%, to an amount of 0.75 to 1  $\text{kgm}^{-2}$ . The curing of the adhesive and of comparison samples was observed by the procedure described in Example 1, and the results are shown in table II, comparison A and B samples having an adhesive thickness of 0.8-0.9  $\text{kgm}^{-2}$  and 1.5  $\text{kgm}^{-2}$  respectively.

TABLE II

GEL CONTENT (%)

Oven Temperature		80°C		120°C	
Time (Minutes)	Heat Shrink	Comparison	Heat Shrink	Comparison	
		A	B	A	B
0	8	8	8	8	8
5	16	7	5	82	12
10	20	7	18	85	13
15	24	10	16	79	50
20	22	10	34	78	57
30	42	10	30	84	58



EXAMPLE 3

An adhesive was prepared by mixing the following particulate components:

		$T_i$	$T_{60}$	Parts by weight
5				
	(a) Polyamide sold under the trade name Macromelt 6301 modified by milling in 10% by weight of a plasticiser sold under the trade name "santicizer 8" by Monsanto	45°C	80°C	9
10				
	(b) Macromelt 6301 polyamide modified by milling in 10% by weight of a polymercaptan sold by Diamond Shamrock under the trade name Capcure 3-800"	70°C	84°C	9
15	(c) Epoxy cresyl novolak resin sold under the trade name "ECN 1280" by CIBA GEIGY	42°C	67°C	59
	(d) dimethylaminopyridine (accelerator)	105°C		3
	(e) Talc			20

The composition was graded to exclude particles greater than 300 micrometres and pressed onto a heat-shrinkable sheet as described in Example 1. Curing of the adhesive was observed by the procedure described in Example 1 and the results are shown in Table III.

TABLE III

Oven temperature = 140°C

	Time	Gel Content (%)	
		Heat Shrink	Comparison
5			(0.8-0.9kgm <sup>-2</sup> ) (1.5 kgm <sup>-2</sup> )
	0	0	0
	5	51	35
	10	50	42
	15	55	52
10	20	49	56
	30	57	55

EXAMPLE 4

50 parts of a cryogenically ground reactive polyamide sold under the trade name "Macromelt 6071" ( $T_i = 52^\circ\text{C}$ ;  $T_{60} = 72^\circ\text{C}$ ) were mixed with 50 parts of a powdered blocked isocyanate sold by Mobay Chemical Co. under the trade name "Mondur SH" ( $T_{60} = 97^\circ\text{C}$ ) to form an adhesive composition. The procedure of Example 1 was repeated with the exception that the extent of cure of the adhesive was determined by measuring the  $T_{80}$  value of the samples of the adhesive after removal from the oven and that an aluminium pan was used for the comparison samples. The results are shown in Table IV.

TABLE IV

TIME (Minutes)  $T_{80}/^{\circ}\text{C}$  (Oven temperature =  $120^{\circ}\text{C}$ )

		Heat Shrink	Comparison ( $1.5 \text{ kgm}^{-2}$ )
5	0	88	88
	5	97,99	
	10	121,123	
	15	120,119	118
	20	136,155	116,126
10	30	205,172	109,180

EXAMPLE 5

150 parts of Macromelt 6301 polyamide that had been modified by milling in 5% by weight of a reactive liquid polyamide sold under the trade name Euredor 115 (formerly called Versamid 115) and had been cryogenically ground to form a powder ( $T_{60} = 74^{\circ}\text{C}$ ) were mixed with 100 parts of a powdered ethylene -vinyl acetate-acid terpolymer sold by du Pont under the trade name Elvax 4260, 80 parts of a bisphenol A epoxy resin sold by Shell Chemicals under the type No. Epikote 1004 ( $T_{60} = 80 - 100^{\circ}\text{C}$ ), and 6 parts of a dimethylaminopyridine accelerator. Each of the components had been sieved to remove all particles greater than 300 micrometres in size.

The adhesive was applied onto a heat-shrinkable sheet and cured as described in Example 1, the curing being measured by the  $T_{80}$  value of the adhesive. The oven temperature was of  $120^{\circ}\text{C}$ . The results are shown in Table V.

TABLE V

Time (minutes)	Heat Shrink	$T_{80}/^{\circ}\text{C}$	
		Comparison (0.8-0.9 kgm <sup>-2</sup> )(1.5 kgm <sup>-2</sup> )	
5	5	94	100
	10		98
	15	107	84
	20	116	109
	30	118	96
			93

10 Example 6

An adhesive was prepared by blending 48 parts of a reactive polyamide (Macromelt 6071) with 3 parts dimethylaminopyridine, then cryogenically grinding the blend to form a powder and sieving the powder to a particle size of less than 300 micrometers. To this were added 34 parts of a powdered multifunctional epoxy cresyl novolak resin sold by Dow Chemicals under the trade name "XD 7855" ( $T_{60} = 69-77^{\circ}\text{C}$ , particle size less than 300 microns), 10 parts of powdered decabromo diphenyl ether (flame retardant) and 5 parts antimony trioxide.

The adhesive was applied onto a heat-shrinkable article and its curing measured as described in Example 1 at an oven temperature of  $140^{\circ}\text{C}$  with the exception that an aluminium pan was used for the comparison samples. The results are shown in Table VI.